Hybrid Encapsulated Ionic Liquids for Post-Combustion Carbon Dioxide (CO_2) Capture

Federal Award No. DE-FE0026465 - David Lang

Joan F. Brennecke
Thomas F. Degnan, Jr.
Mark J. McCready
Mark A. Stadtherr
Dept. of Chemical and Biomolecular Engineering
University of Notre Dame
Notre Dame, IN 46556 USA

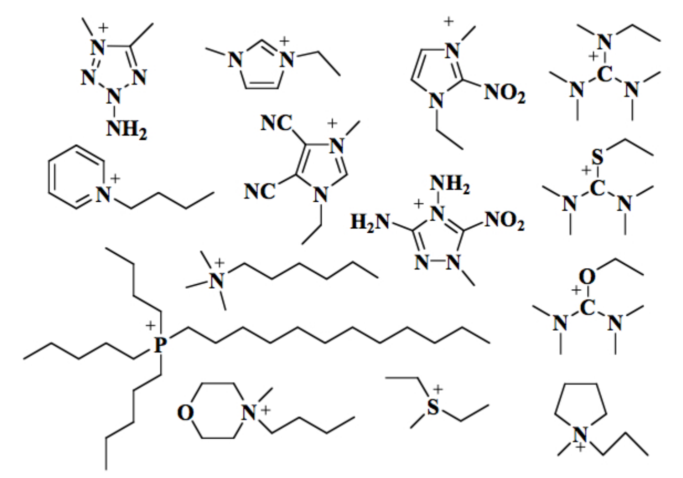
August 24, 2017
Project Initiation: 10/1/15

Partner: Joshuah K. Stolaroff
Lawrence Livermore National Laboratory

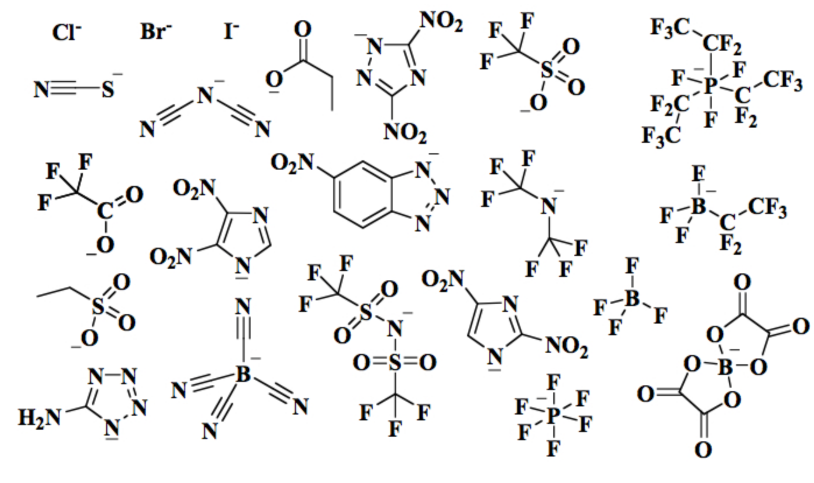
Ionic Liquids

- Pure salts that are liquid around ambient temperature
  - Not simple salts like alkali salts
- Many favorable properties
  - **Nonvolatile**
  - Anhydrous
  - High thermal stability
  - Huge chemical diversity

Examples of cations

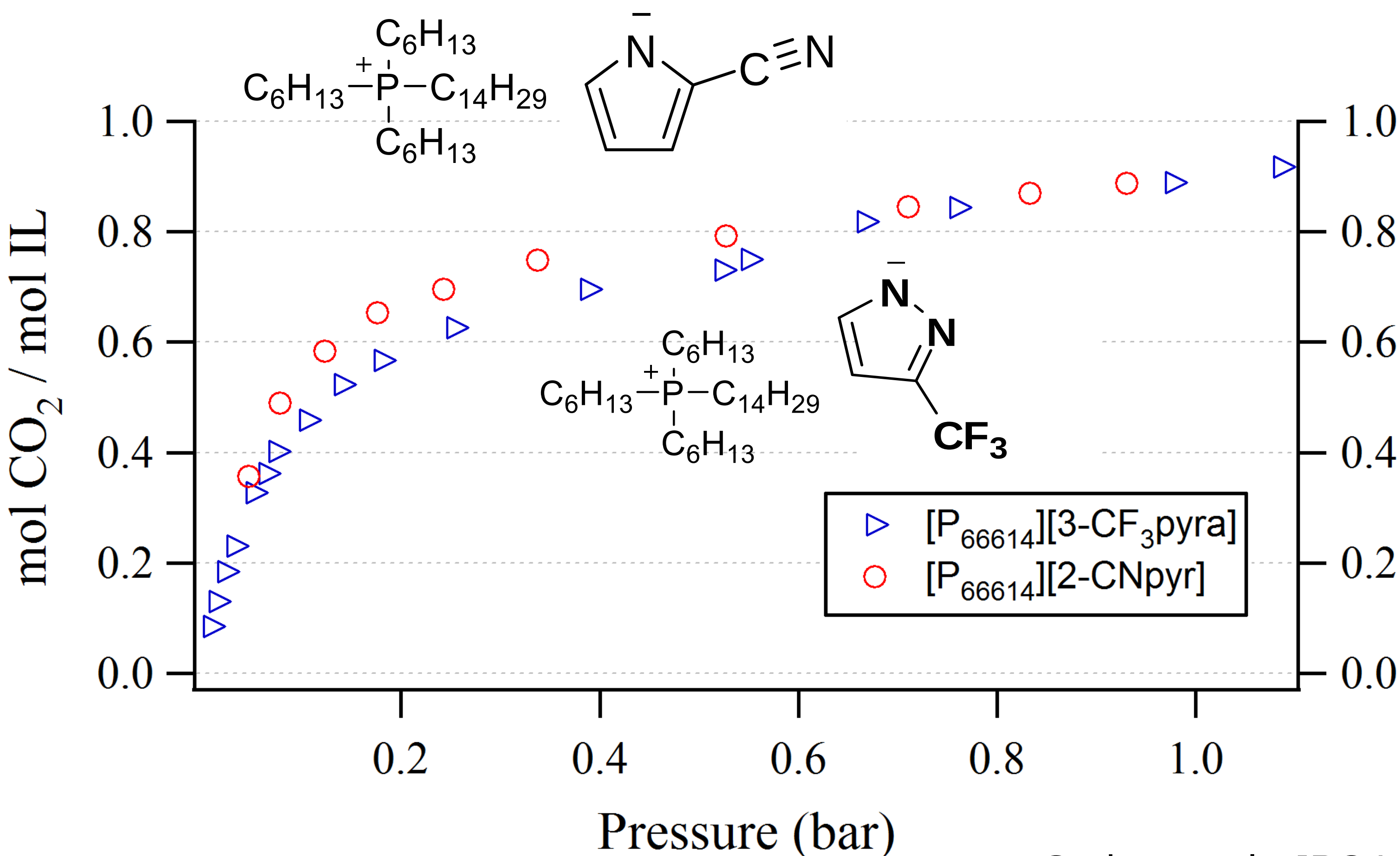


Examples of anions



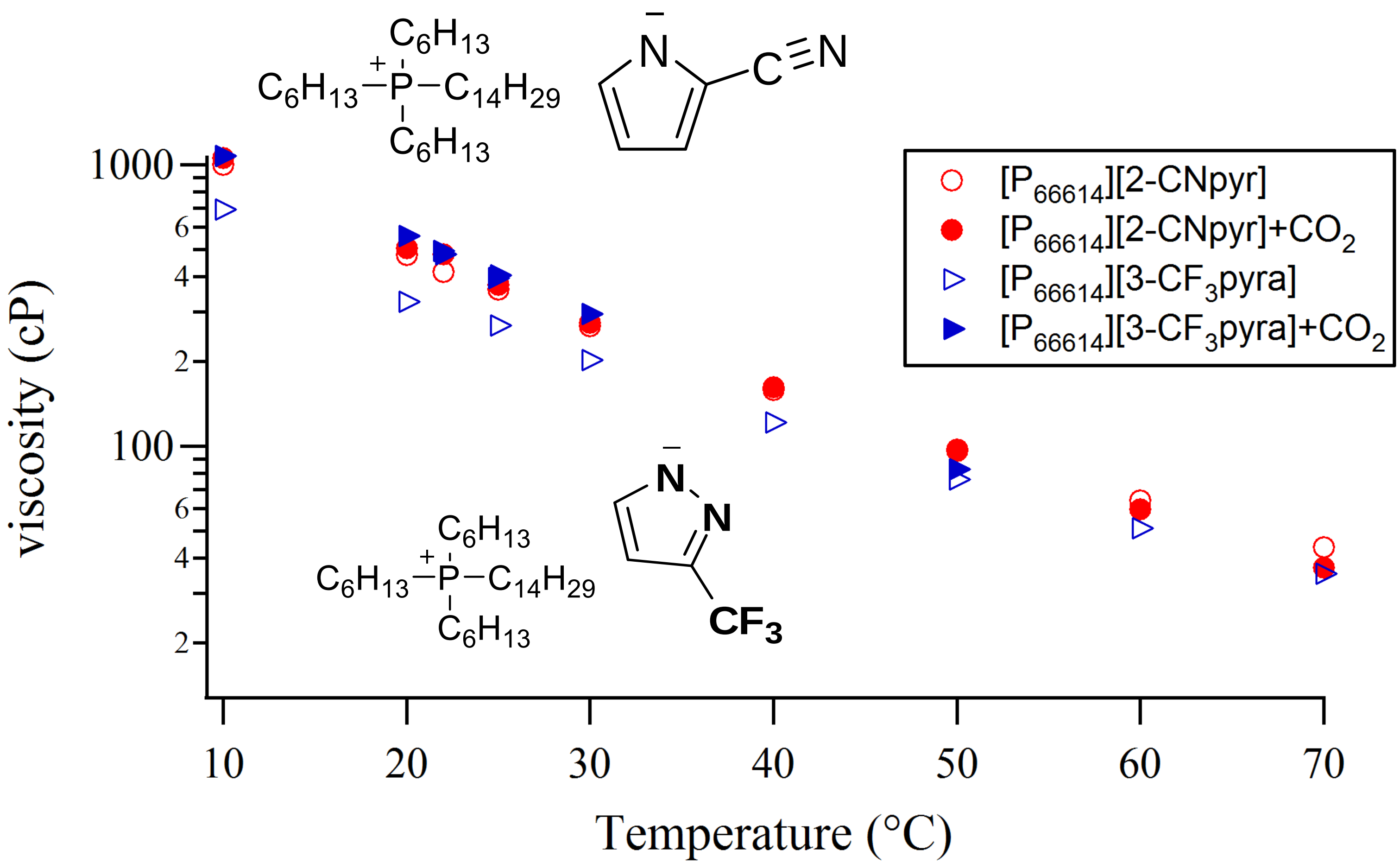
AHA – aprotic heterocyclic anions

- Retain amine in ring structure
- Further reduce free hydrogens to reduce hydrogen bonding



Gurkan et al., JPC Lett, 2010

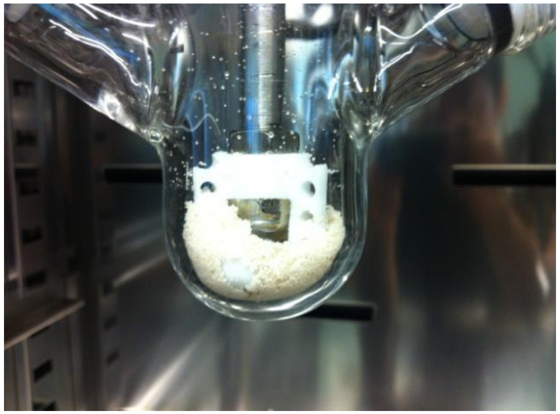
Eliminate Viscosity Increase by Using AHA – aprotic heterocyclic anions



Gurkan et al., JPC Lett, 2010

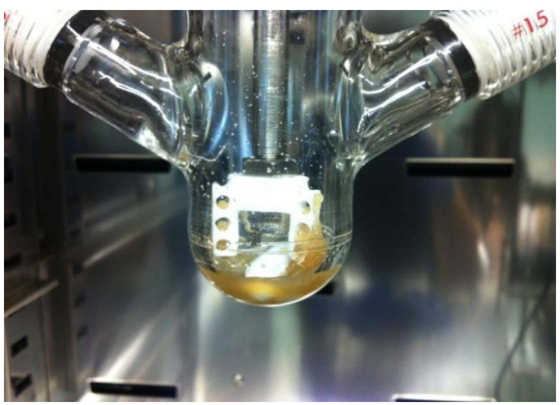
Phase Change Ionic Material

70 °C

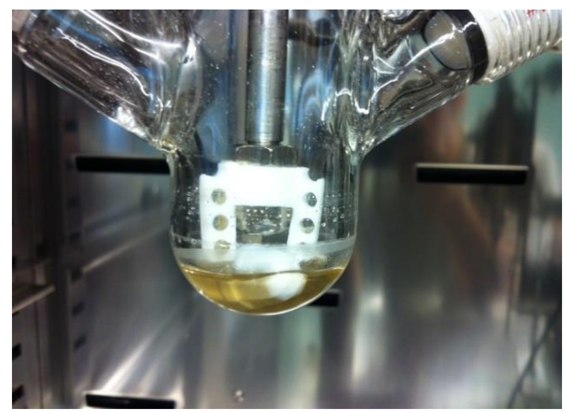


Pure material; T_m=166 °C; no CO_2

60 mbar CO_2



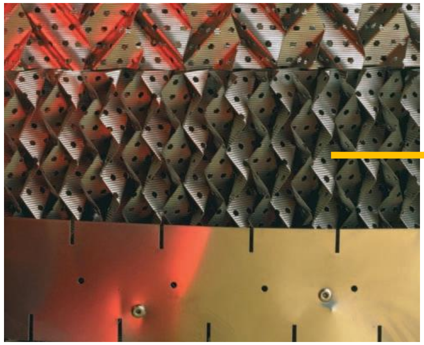
100 mbar CO_2



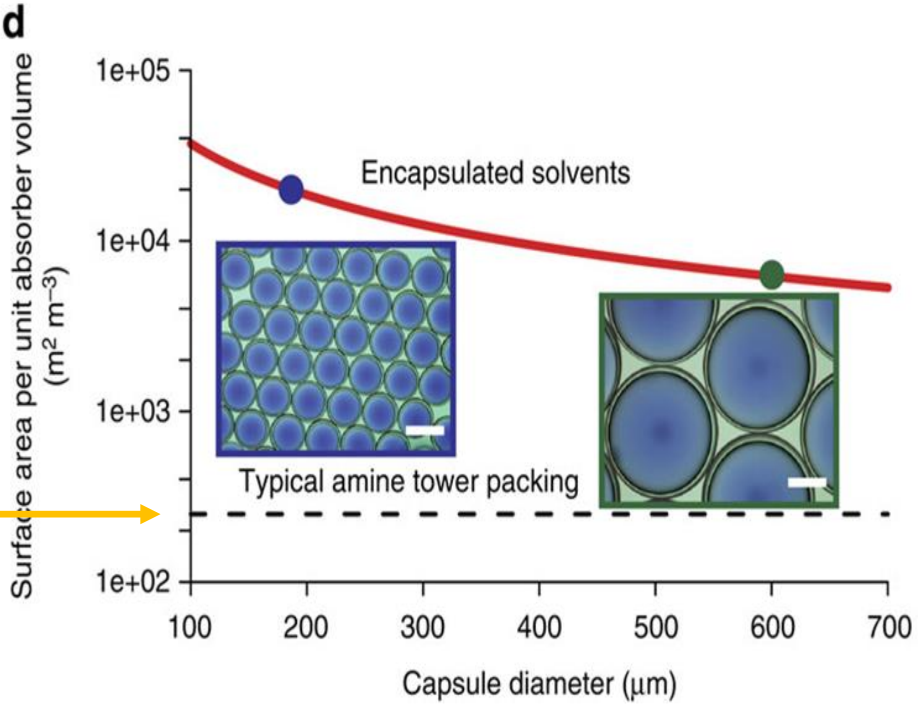
150 mbar CO_2

Microencapsulation

- Idea
  - Improve mass transfer by increasing gas-solid (liquid) contact AREA
  - Decrease column size
  - Decrease capital costs



Random and structured packing



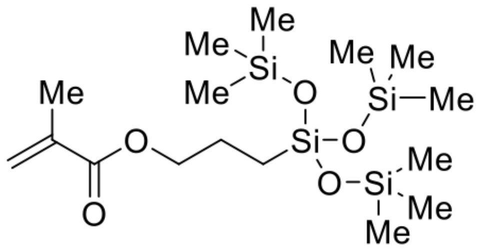
Vericelli et al., 2014

Selection of ILs and PCILs

- Chose one IL and one PCIL
  - NDIL0230
  - NDIL0309
- Criteria
  - Melting point
  - Thermal stability
  - Enthalpy of reaction with CO_2 between -45 and -60 kJ/mol
  - Viscosity
  - $T_m^{complex} < T_m^{pure}$ for PCIL

Microencapsulation

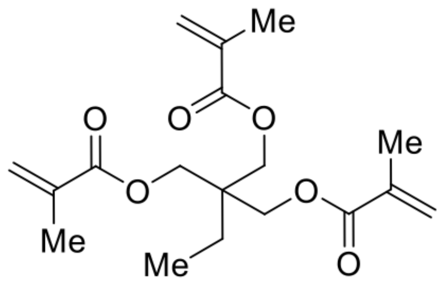
Active Monomer



SiTRIS

3-[Tris(trimethylsiloxy)silyl]propyl methacrylate

Crosslinker

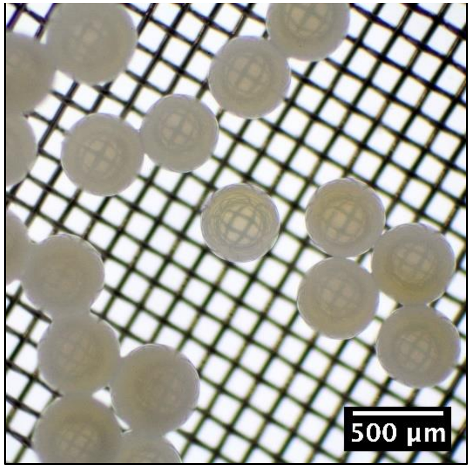


TMPTMA

Trimethylolpropane trimethacrylate

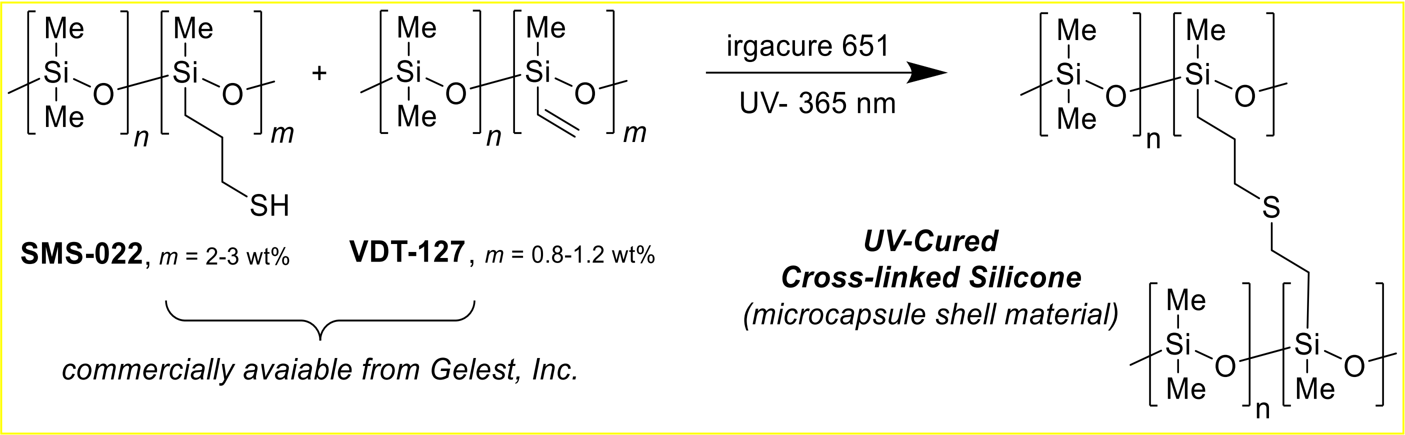
Scheme 1: Formulation of SiTRIS shell material

- LLNL produced encapsulated IL
- Reported last year
- Unfortunately, shell material deactivated the IL

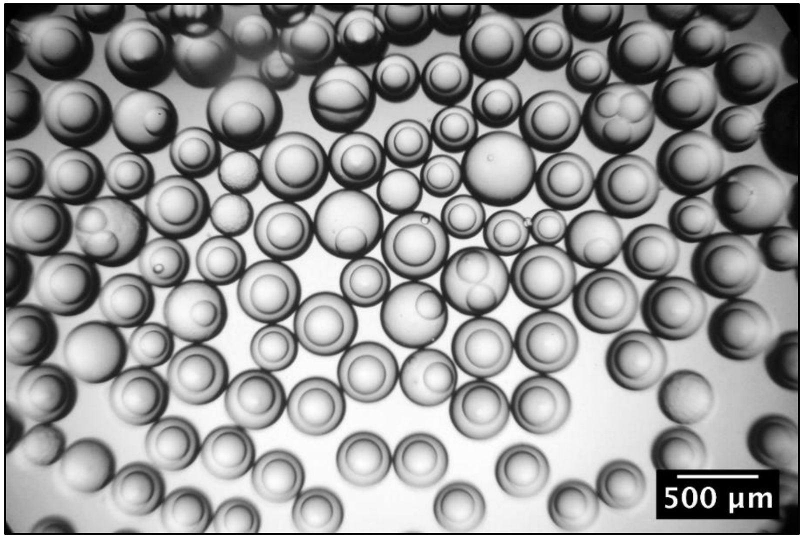


NDIL0230 encapsulated in SiTRIS

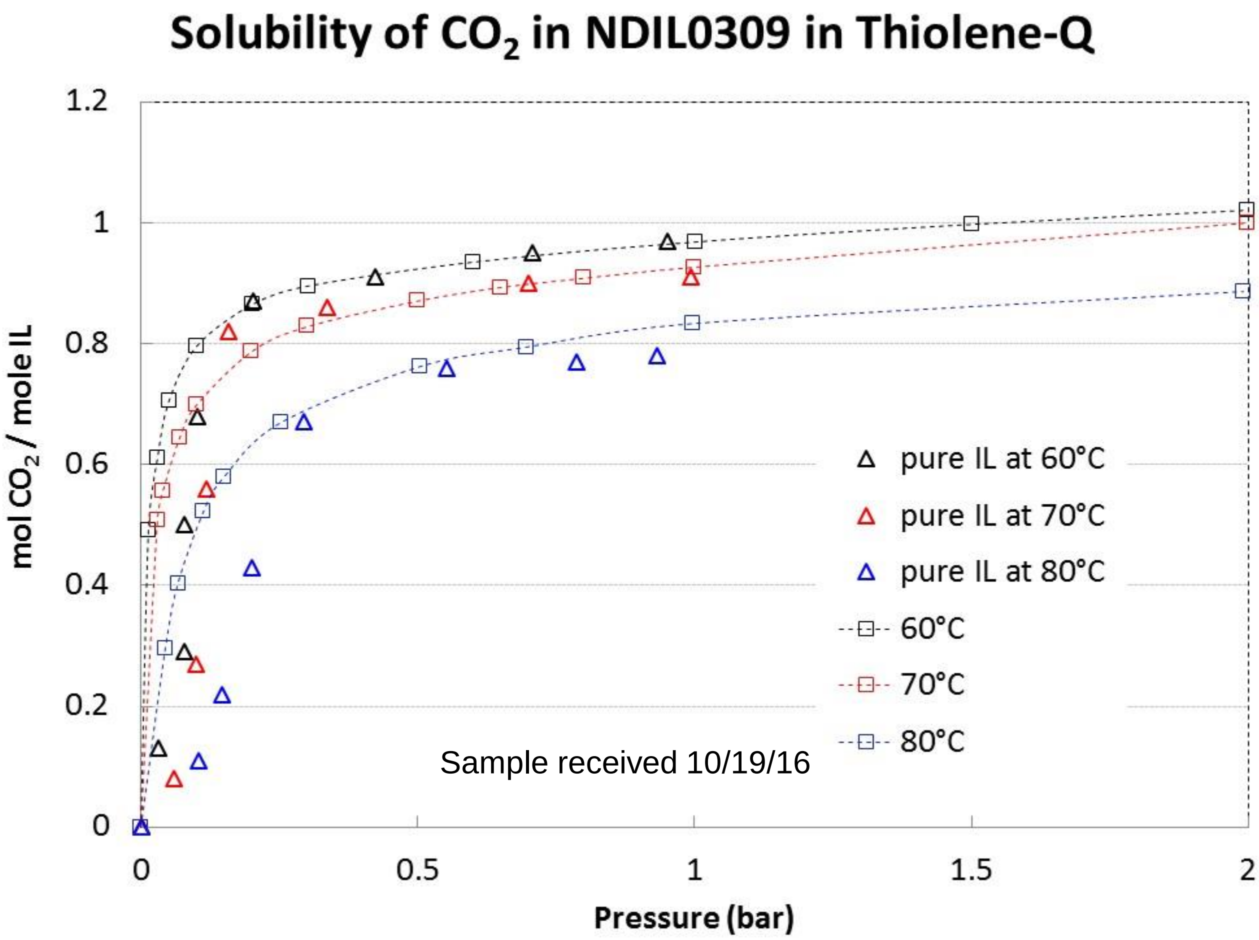
Microencapsulation



- LLNL developed and refined ThioleneQ shell material formulation
- Chemical compatibility with NDIL0230 and NDIL0309 established
- Alternative crosslinker identified for improved NDIL0230 production and in-air production



Thermodynamic testing (of encapsulated PCIL)

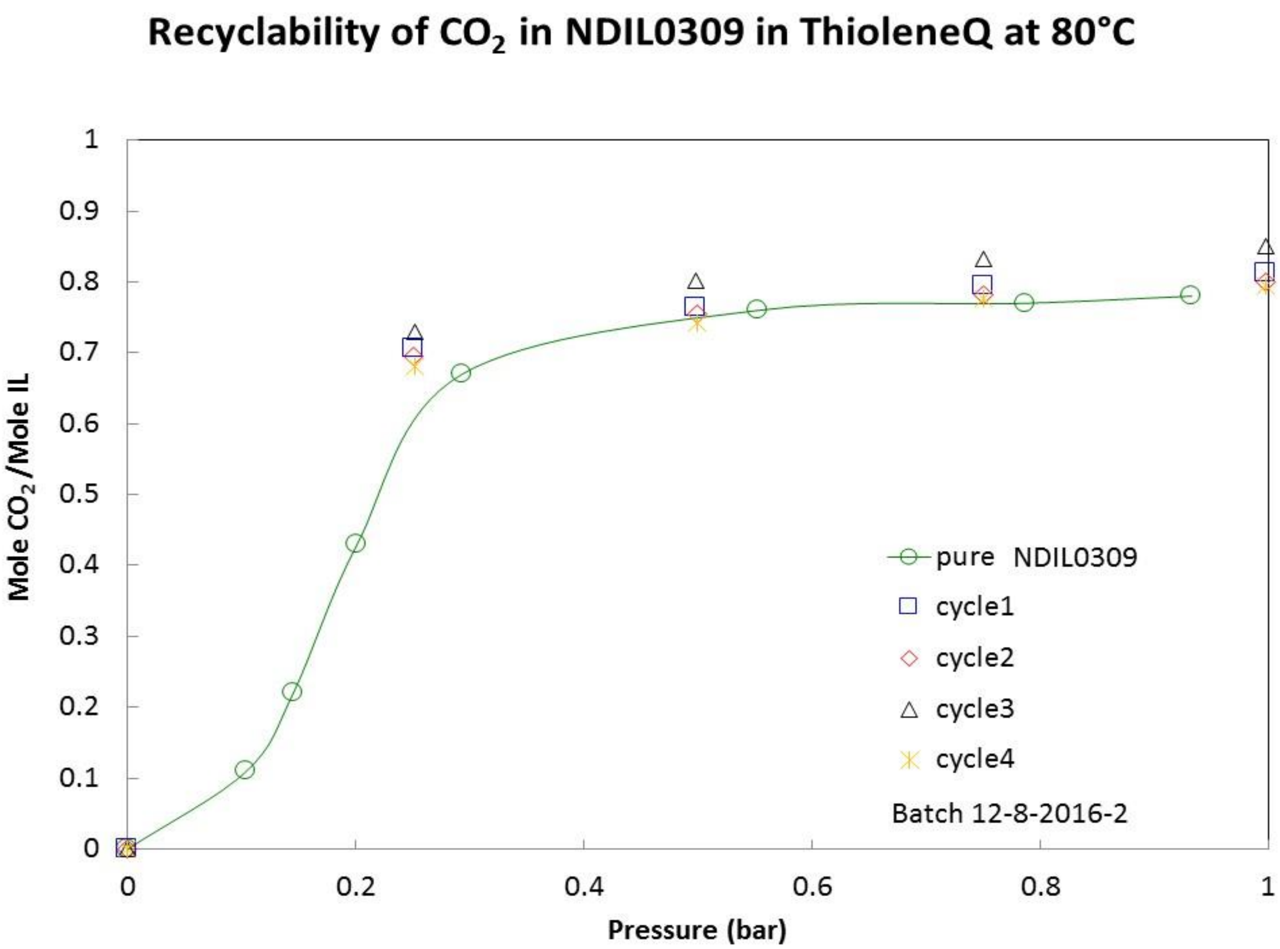


Corrected for physical CO_2 uptake by shell material

Meets CO_2 uptake criterion

- Excellent agreement in CO_2 capacity and no degradation

Thermodynamic testing (of encapsulated PCIL)

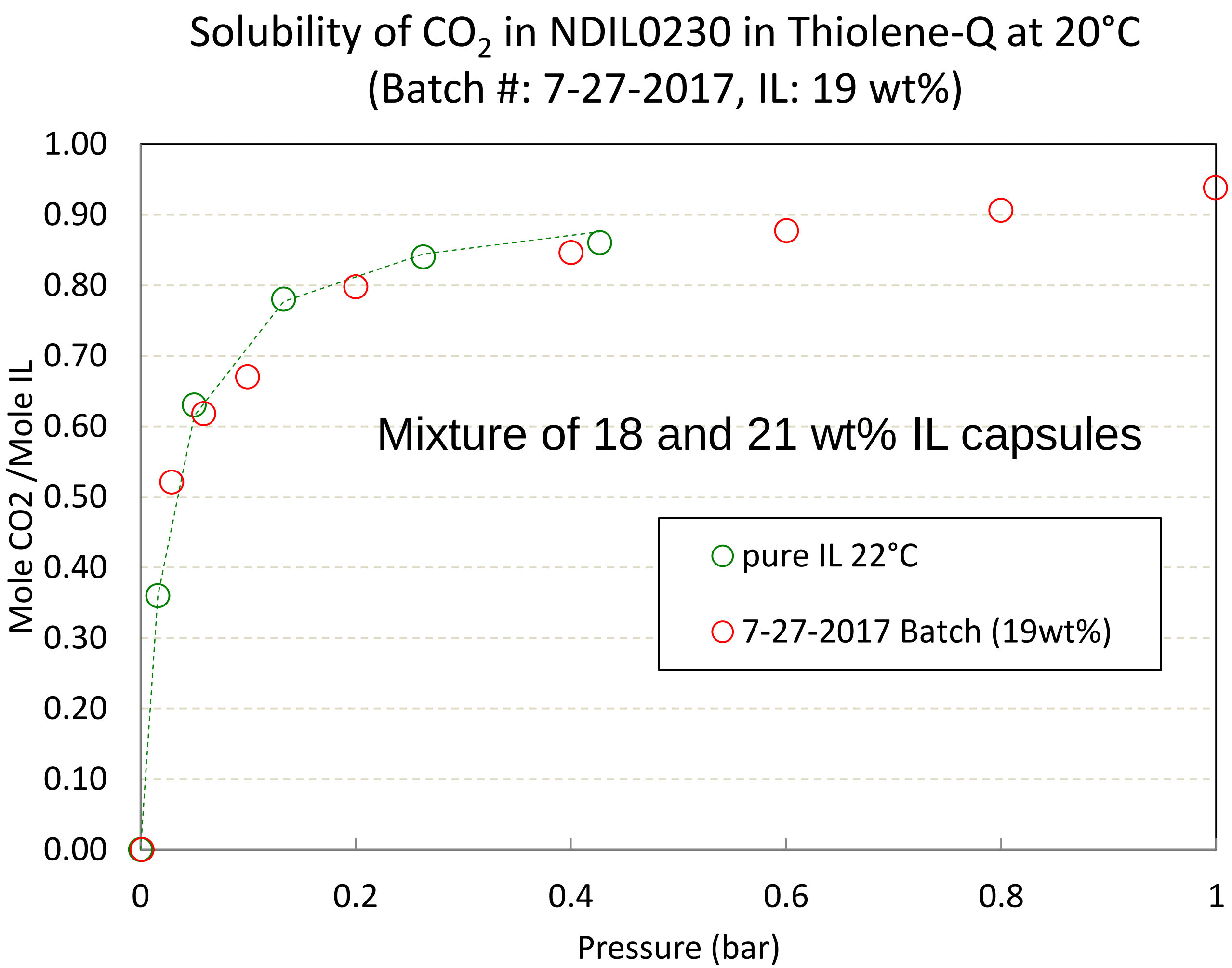


Corrected for physical CO_2 uptake by shell material

Meets CO_2 uptake criterion

- Excellent recyclability

Thermodynamic testing (of encapsulated IL)

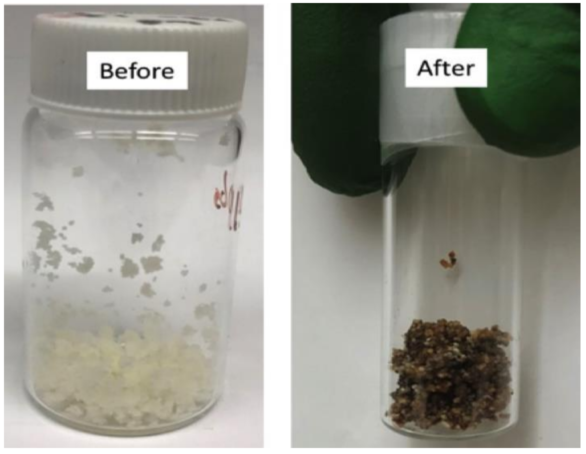


Corrected for physical CO_2 uptake by shell material

Meets CO_2 uptake criterion

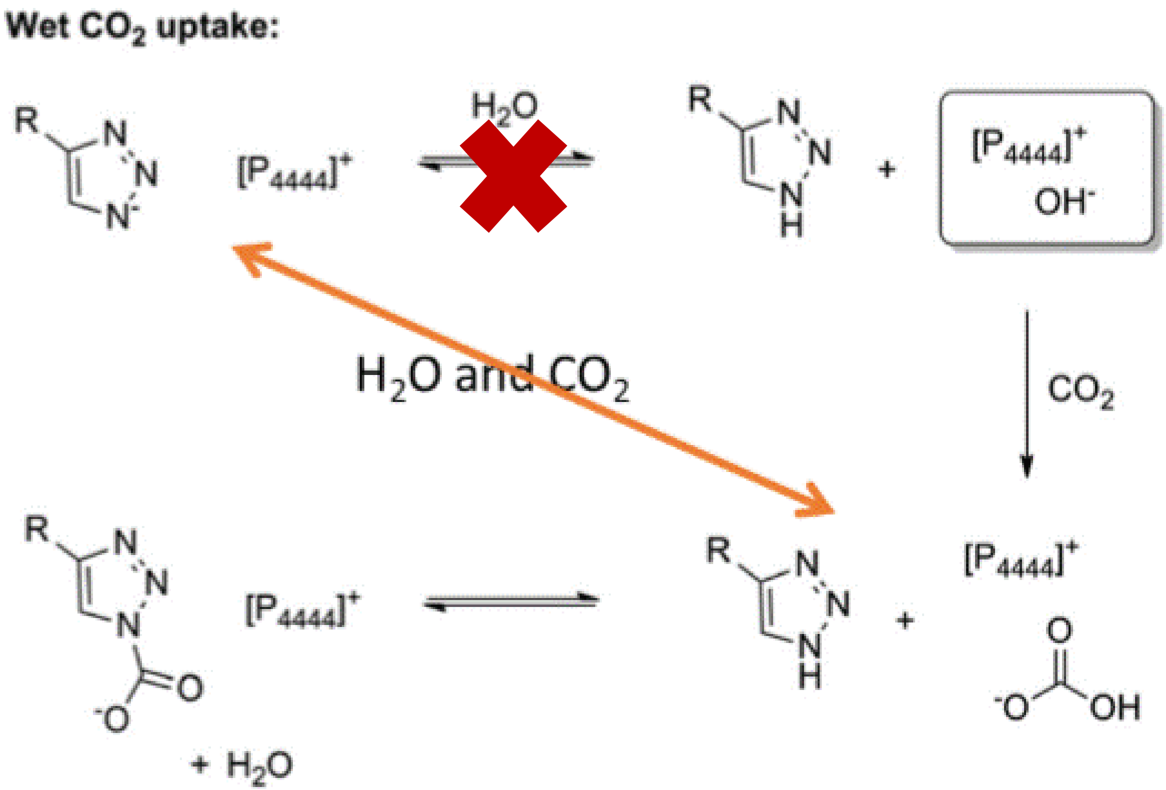
Effect of Impurities

- Both NDIL0230 and NDIL0309 react irreversibly with SO_2 and NO_x
- Both free IL/PCIL and encapsulated
- CO_2 capture with IL or PCIL would need to be after the FGD and NO_x reduction units



Effect of Impurities - Water

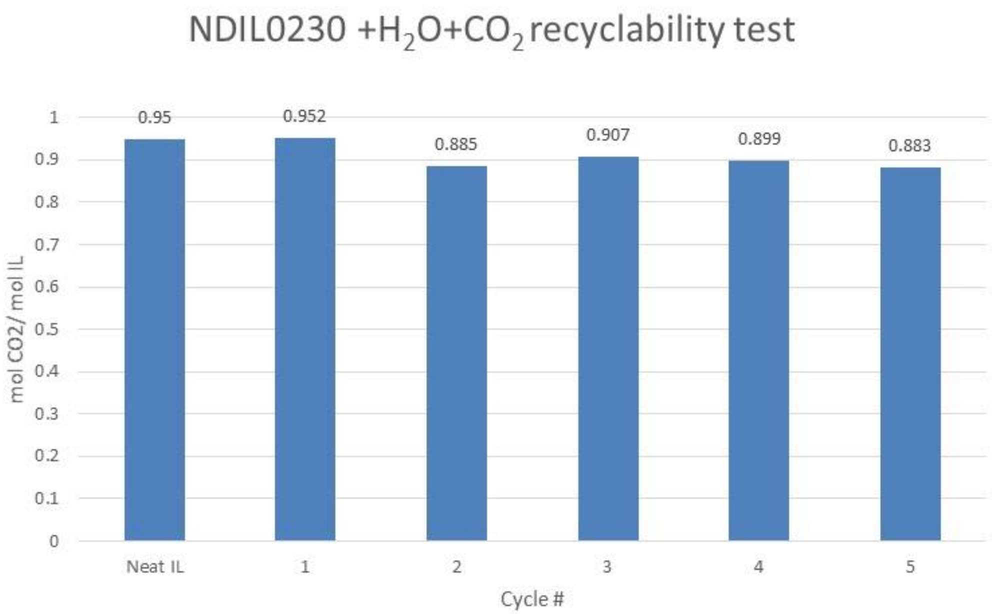
Possibility of reprotonation and bicarbonate formation

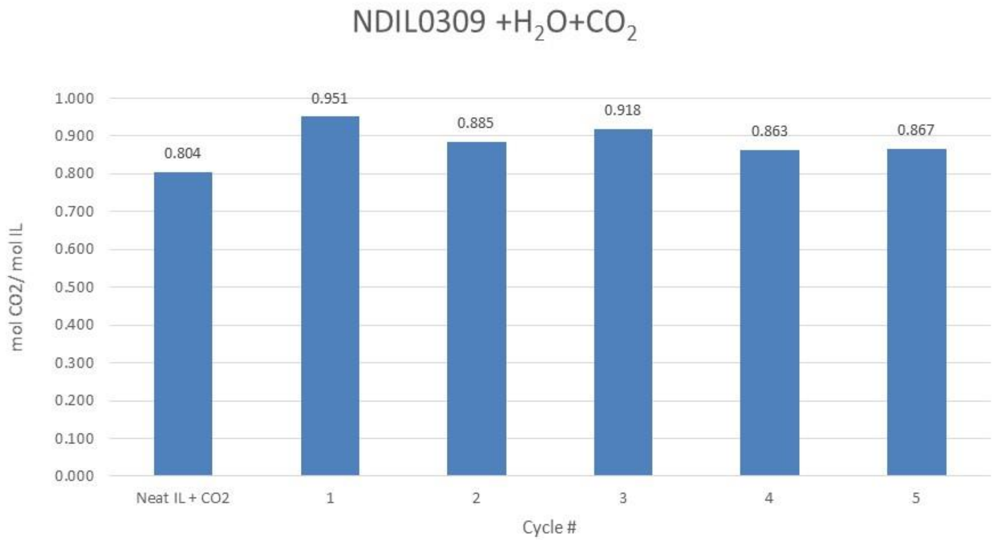


Eliminated from consideration ILs that reprotonated just in presence of water

Adapted from Thompson et al., RSC Adv., 2014, 4, 12748

Effect of Impurities - Water



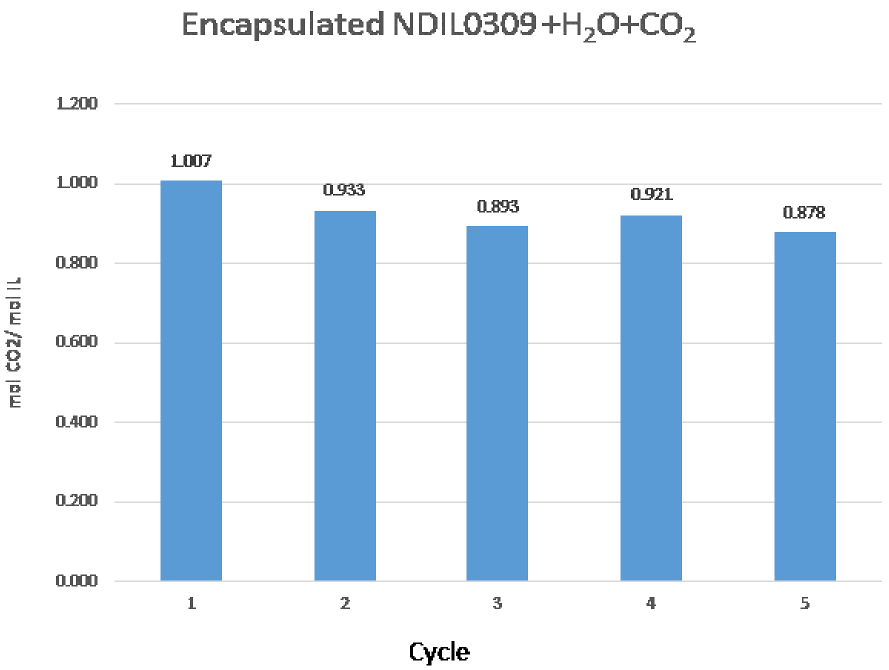


Reaction of water with IL/PCIL in the presence of CO_2 is completely reversible and recyclable!

Do not need to exclude water from the core of the microcapsules

Effect of Impurities - Water

Also true for encapsulated PCIL



Reaction of water with PCIL in the presence of CO_2 in capsules is completely reversible and recyclable!

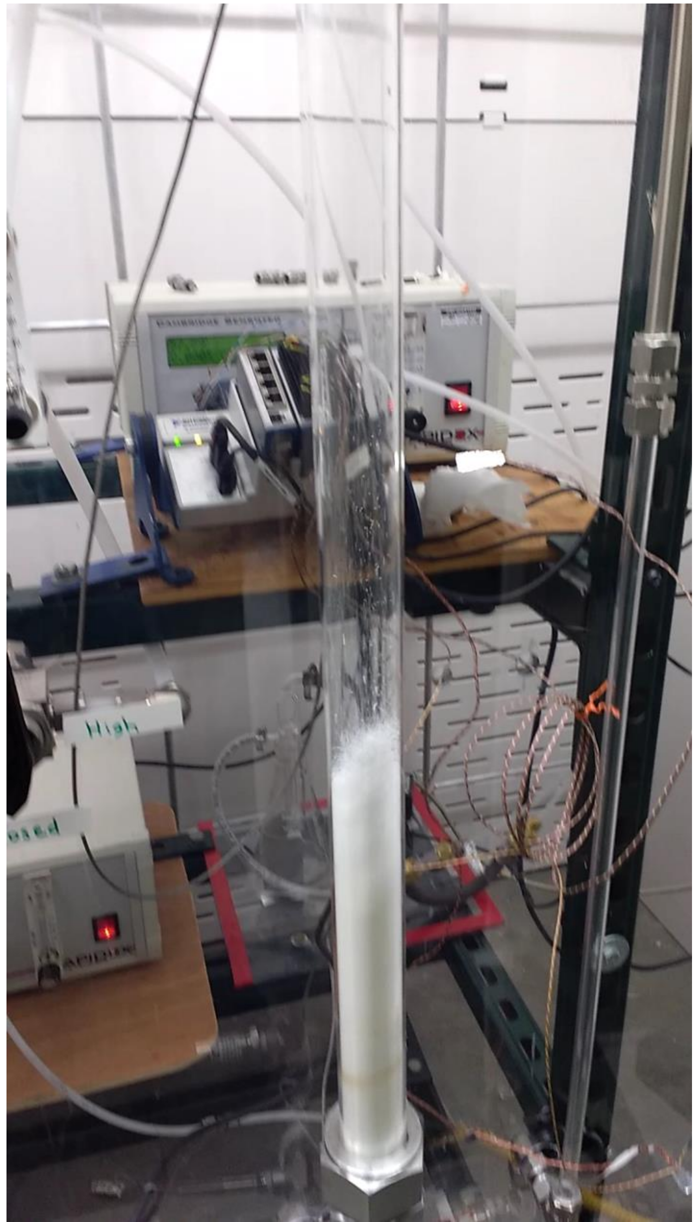
Do not need to exclude water from the core of the microcapsules

Laboratory Scale Unit

- Design, construction and shake-down
- Absorption and stripping
- Located in walk-in hood
- Interchangeable columns
- 1, 3, 6 cm diameter thus far

Laboratory Scale Unit

- Video of capsules in 6 cm column, V = 12 cm/s



11.1d:Pressure transducers: Pressure fluctuations give insight into fluid mechanics of gas-solid flow

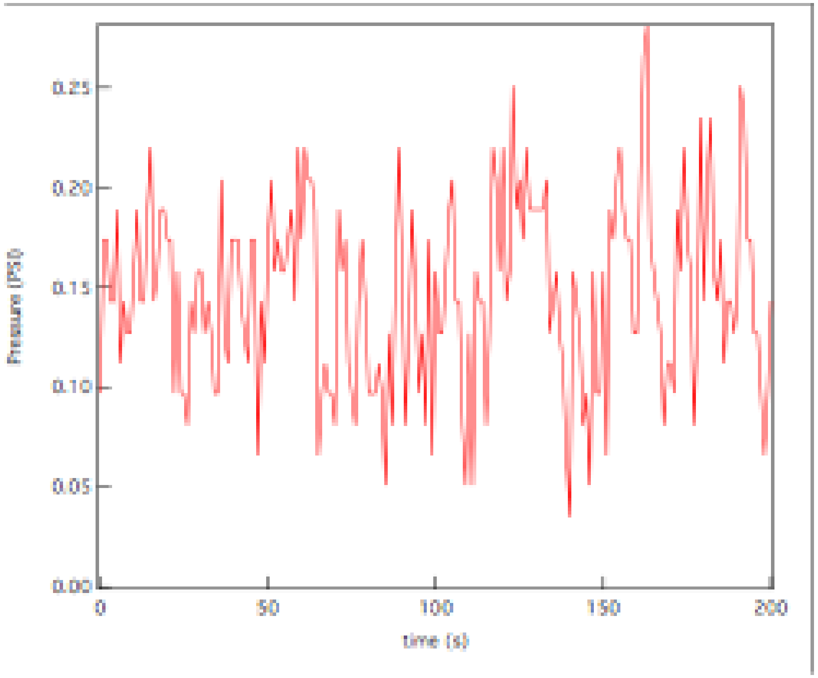
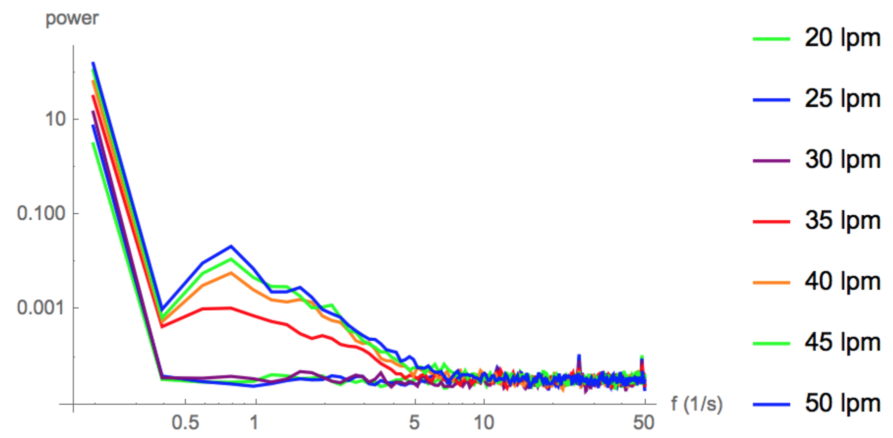


Figure 42: Pressure fluctuations during a fluidization tes



Power spectra as a function of flow rate

LSU – Mass Transfer Measurements

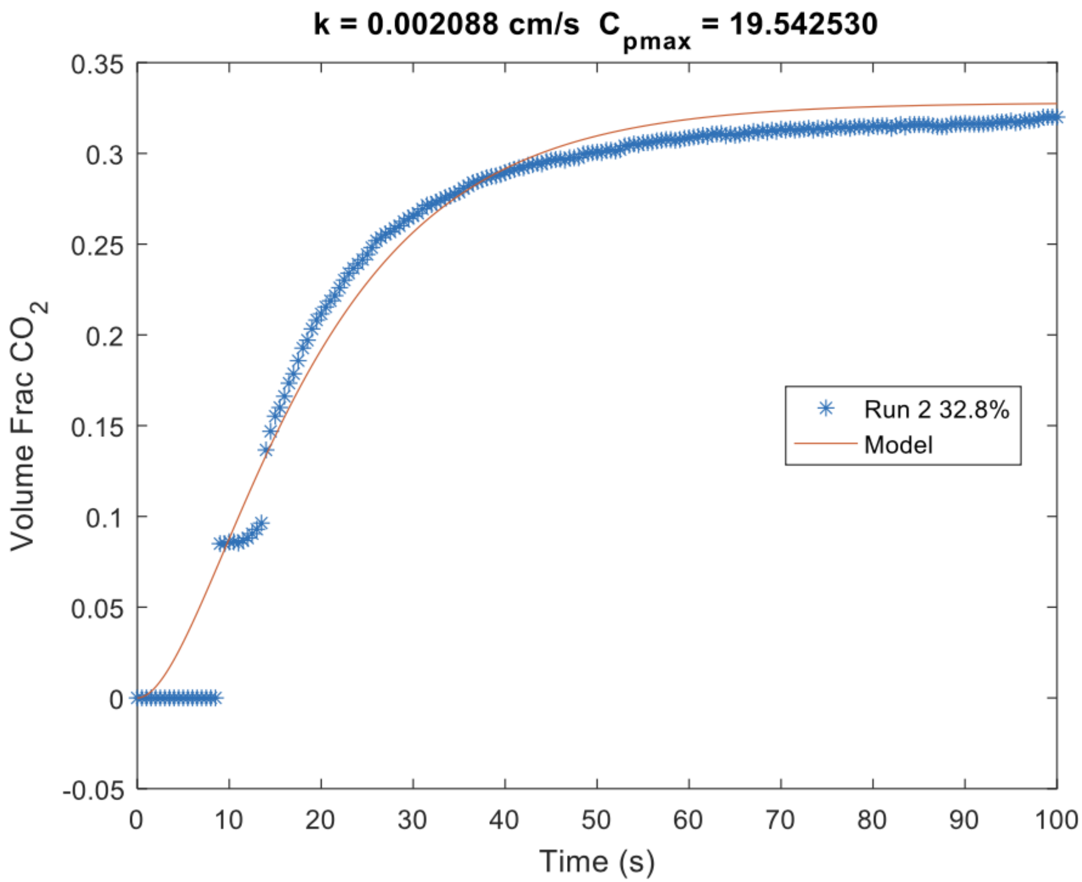


Figure 14: Volume fraction of CO_2 absorbed vs. time (sec) for Thiolene-Q capsules filled with NDIL0309.

LSU – Mass Transfer Measurements

Total Flow Rate (liters/ min.)	Composition (vol % CO_2)	P_{Co2} (bar)	Temp (C)	Absorption Time (s)	Regen-eration Amount (L CO_2)	(mol CO_2)	Regen Temp (C)	mol ratio	k (cm/s)
3.3	45.67	0.547	71	1236	0.229	0.0096	114	0.65	1.5E -05
3.3	44.55	0.537	73	433	0.224	0.0094	106	0.64	2.2E -04
3.3	45.93	0.561	78	733	0.23	0.0096	109	0.66	3.1E -05
3.3	44.74	0.533	69	673.5	0.228	0.0095	108	0.65	8.8E -05
3.3	45.22	0.542	71	356	0.243	0.0101	114	0.69	1.0E -04

Recyclability (5 cycles) shows consistent CO_2 capacity of 0.66 +/- 0.02 moles CO_2/mol PCIL

Rate Based Model

- Developed rate-based model of absorber and stripper
- Used mass transfer data from Laboratory Scale Unit to evaluate model performance
- Incorporated multi-objective optimization and sensitivity analysis capabilities into rate-based model
  - Understand sensitivity
  - Predict best operating conditions

Rate Based Model

- Comparison of measured vs. predicted mass transfer flux in a fluidized bed of microcapsules containing NDIL0309

Measured mass transfer flux (mol/(m^2·s))	Predicted mass transfer flux (mol/(m^2·s))
4.84×10^{-4}	3.33×10^{-4}

True prediction (no adjusted parameters)

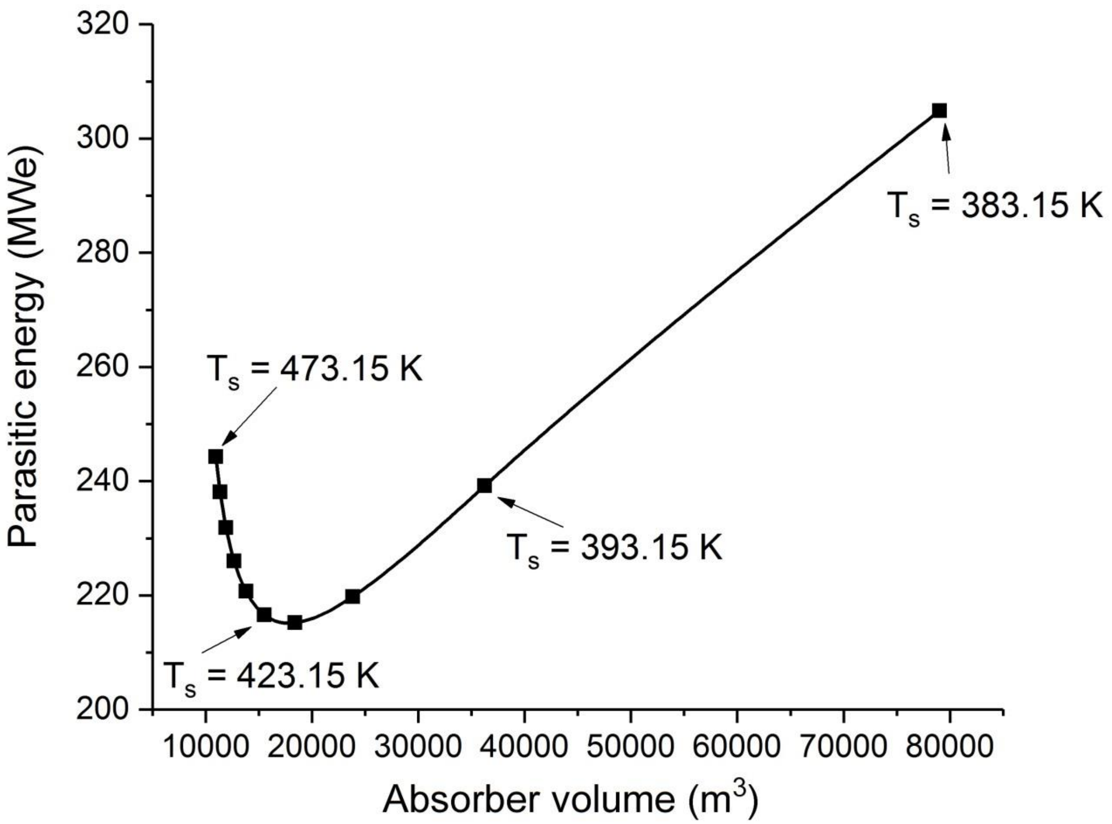
Excellent agreement

Confidence in model

- Absorption temperature = 70 °C; Capsule diameter = 560 μm; Exposure time = 100 s

Rate Based Model

- Sensitivity Analysis Example – Stripper Temperature



T_a = 293.15 K,
P_a = P_s = 1 bar

ΔH_{chem} = −45 kJ/mol,
ΔS_{chem} =−122 J/(mol K),
μ = 100 cP
d_{mc} = 200 μm
ε_{ex} = 0.99

- A “Pareto curve”

Summary

- Successful encapsulation of ILs and PCILs
- Reaction with water in presence of CO_2 completely reversible so no need to exclude water from capsules
- Successful fluidization and absorption/ desorption cycling of encapsulated NDIL0309 in LSU
- Rate-based model predictions of mass transfer flux close match to experimental values

Future Work

- Scale-up and production of kg quantities of encapsulated IL and PCIL
- Testing of kg quantities in laboratory scale unit
- Investigation of effect (if any) of reaction with water on process energy consumption
- Process modeling and economics (not full techno-economic analysis)

Acknowledgments

- David Lang
- DOE Federal Award No. DE-FE0026465